

Title: DEVELOPMENT OF IMPROVED CATALYSTS FOR THE SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDES WITH HYDROCARBONS

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ABSTRACT

Significant work has been done by the investigators on the cerium oxide-copper oxide based sorbent/catalysts for the combined removal of sulfur and nitrogen oxides from the flue gases of stationary sources^(1,2). A relatively wide temperature window was established for the use of alumina-supported cerium oxide-copper oxide mixtures as regenerable sorbents for SO₂ removal. Evaluation of these sorbents as catalysts for the selective reduction of NO_x with methane gave promising results leading to NO conversions between 10 to 17% in the temperature range 375°C – 475°C at the space velocity used in the experiments (13700/hr).

The current research aims to improve the performance of the cerium oxide-copper oxide based catalysts with a three-pronged approach. The investigation of the reaction mechanism, the first component, will help in the selection of promoters to improve the catalytic activity and selectivity of the sorbents in the SCR with methane. This will result in new catalyst formulations (second component). The third component of the project is to develop an alternative SCR process using another inexpensive fuel, residual fuel oil, instead of natural gas. The industrial partner, TDA Research, will evaluate the long- term stability and durability of the selected sorbent/catalysts.

Promoted catalysts were prepared by impregnation (by the incipient wetness technique) of the original supported copper oxide-ceria catalysts by the aqueous solution of the corresponding metal salts, namely rhodium(III) chloride and manganese(II) nitrate.

In the investigation of the mechanism of selective catalytic reduction reaction, Temperature-Programmed Desorption (TPD) and Temperature Programmed Reaction (TPRx) experiments were performed. For temperature-programmed experiments, a Micromeritics Pulse Chemisorb 2705 with TPD/TPR Option is used. A mass spectrometer-gas chromatograph system (SATURN 2000MS/3800GC) from Varian is used for the identification of desorbed species and reaction products. Experiments done to date produced significantly different TPD and TPRx results for the promoted and unpromoted catalysts indicating different reaction mechanisms.

For NO_x reduction experiments, the prepared catalyst spheres were ground and a particle size range of 250 - 425 μm was used for the tests in a quartz microreactor. The reactant gas mixture is prepared from high purity bottled gases without further purification using flow control valves. Experimental variables in a standard SCR experiment were as follows:

temperature	= 473 - 798 K
methane/NO ratio	= 1.0
concentration of O ₂	= 1.5 %
concentration of H ₂ O	= 0-7 %
concentration of SO ₂	= 0-3000 ppm
total gas flow rate	= 750 cc/min
catalyst amount	= 2 g

A typical reactant gas composition was 800 ppm NO, which contained 1.5% O₂, 7% H₂O, methane as reductant (reductant/NO = 1), and the balance He.

Gas samples were analyzed using a Varian 3400 Gas Chromatograph for CO, CO₂, N₂, O₂ (with TCD detector) and Thermo Environmental Instruments Model 42H Chemiluminescence NO-NO₂-NO_x analyzer for NO and NO₂.

The NO reduction activity of the catalysts with higher Cu/Ce ratio (Cu/Ce=3) remained the same when promoted by rhodium compared to the activity of the unpromoted catalyst. However, manganese was an effective promoter, increasing the activity of these catalysts by 32 % compared to that of the unpromoted catalyst.

Promotion with both rhodium and manganese increased the activity of the catalysts having lower Cu/Ce ratio (Cu/Ce=1/3), resulting in 25 % and 43 % increase in conversion. The effects of other promoters are currently being investigated.

A poster paper, entitled "Selective Catalytic Reduction of NO_x by Hydrocarbons on Supported Copper Oxide-Cerium Catalysts" was presented at the 17th North American Catalysis Society Meeting at Toronto, Canada on June 3-8, 2001. A paper entitled "Investigation of Mixed Oxide Catalysts for the Selective Catalytic Reduction of NO by Methane and Propylene" was presented at the AIChE 2001 Annual Meeting at Reno, Nevada on November 4-8, 2001. Anthony Samuels, an undergraduate researcher made a presentation entitled "Selective Catalytic Reduction with Hydrocarbons" at the AIChE Mid-Atlantic Regional Conference at Virginia Tech, Blacksburg, VA on March 15-17, 2002.

References:

1. **J.F. Akyurtlu and A. Akyurtlu**, "Investigation Of Combined SO₂/NO_x Removal By Ceria Sorbents," Final Report for DE-PS22-92MT920 (1996).
2. **J.F. Akyurtlu and A. Akyurtlu**, "Behavior of Ceria-Copper Oxide Sorbents under Sulfation Conditions", *Chemical Engineering Science* **54**, pp. 2991-2997 (1999)